Standard Operating Procedures for the Handling and Analysis of Passive Ozone Samplers

1.0 Introduction

This Standard Operating Procedure (SOP) document contains the procedures for handling the Ogawa passive ozone samplers and details on the analysis and quality control procedures. Also, included is the schedule for reporting results, the format for the data reports, and information requirements for the final report.

Passive ozone samplers are used on a project basis for the determination of integrated ozone exposures at different Park locations. The exposure locations are not limited to the Parks where continuous ozone monitoring is being conducted, nor to our current monitoring sites. The exposure periods for the passive samplers may be from 1 day to 4 weeks, but will typically be 1 week.

The experimental design will be determined based on the objectives of each project, but will typically consist of a monitoring site co-located with a continuous ozone monitor and any number of additional passive monitoring sties within a Park. Duplicate samplers will be exposed to ambient air at each monitoring site. Field blanks (approximately 10% of the total samplers) will be used to determine background nitrite levels on the samplers.

2. Schedule

The passive sampler filters will be purchased by the Contractor from Ogawa and shipped directly to Contractor where they will be loaded into the sampler holders. The Contractor will package and label the samplers prior to shipment to the park contact people. Park personnel will unpack and deploy the samplers according to a schedule provided to them. A form will be included with each sampler to record exposure times, samples labels, events, and locations. After the completed exposure period, the park personnel will return the passive samplers to their shipping containers and return the samples to the Contractor. The samples will be analyzed using ion chromatography at the Contractor's lab according to procedures described in section 3.

Note that extra samplers will be shipped to the parks to cover problems that occur from handling, but the extra samplers will not be analyzed except as additional blanks or when they were exposed to ambient air as substitutes.

2.1. Overall Schedule of the Project

Project schedules are determined on an individual basis. These will be outlined in documents provided for each project. Typically, loaded passive samplers would be shipped by the Contractor one week before the scheduled sampler exposure date. After exposure of the samplers, they would be returned to the Contractor for analysis.

2.2. Shipping Dates for Samples

A complete list of shipping dates and expected return dates will be provided for each project.

3. Sampler Coding and Handling

3.1. Procedures for Loading and Handling Ogawa Devices

Document from the Harvard School of Public Health (HSPH):

Protocols for Ozone Measurement Using the Ogawa Passive Sampler
Revision 1.2 July 10, 1992

The Ogawa passive sampler was originally intended to sample for nitrogen oxides. By using a specific filter coating solution designed at the Harvard School of Public Health (HSPH), the sampler may also be used to monitor ambient ozone. The coating solution is nitrite-based. ozone oxidizes the nitrite on the filter to nitrate, and after exposure, the filter is extracted and analyzed by ion chromatography for nitrate ion.

Note that these protocols assume that precoated filters, available from Ogawa and Co., USA, Inc., will be used. An appendix following the protocols lists the supplies (and their vendors) referred to in this document. If further elaboration is needed for issues discussed in this protocol, please contact Ogawa and Co. Confirm revisions to this protocol with Ogawa before using the ozone samplers.

Part I. Assembly of the Ogawa Sampler Using Precoated FIlters

Equipment

The following is a list of equipment that will be needed at a field site or central laboratory for the preparation of the Ogawa sampler for ozone monitoring.

Forceps, blunt for filter handling
Forceps, sharp with curved tip
Glovebox or plastic glovebag
Lint-free paper wipes (Kimwipes), large & small
Filter paper sheets for glovebox flooring, 18" x 24"
Ultrapure water (Millipore's Milll-Q water (MQ) or equivalents
Coated glass fiber filters (14 mm dia., 2 per sampler)
Ogawa passive samplers:
- sampler body (with z pairs of spacer pads & rings)
- diffusion endcaps (2 per sampler or 1 per side)
- stainless screens (4 per sampler, or 2 screens per side)
- extra stainless screens

masking tape.

New tape will have to be used as necessary to ensure a tight seal. If the sleeve seams on the glovebox tear, use needle and thread to sew them closed.

Cleaning the Sampler Components

The steps outlined below refer to routine sampler cleaning between successive field uses. When the Ogawa

samplers are new, the same steps are taken initially; however, the sampler bodies, spacer pads, and spacer rings must be thoroughly washed in separate groups with Milli-Q water.

All parts of the Ogawa passive sampler must be clean and completely dry before assembling the sampler. After cleaning, lay the parts on Kimwipes to dry. While drying, cover with a large Kimwipe to prevent dust/dirt from settling on the clean parts.

1. Disassemble the samplers and set aside the cylindrical bodies to be cleaned separately.

2. Rinse the endcaps and pin-clips with Milli-Q water, then set the parts on Kimwipes to dry. It may be necessary to tap the water out of the holes in the endcaps in order for them to dry completely.

3. The cylindrical bodies must be wiped clean with a Kimwipe moistened with Milli-Q water. Afterwards, they must be wiped with a dry Kimwipe to absorb any excess water.

4. The stainless screens must be placed in a beaker, then rinsed several times with Milli-Q water. Fill the beaker again with Milli-Q water and place it in a sonication bath for cleaning. Sonicate the screens for 5 minutes, then rotate the beaker a quarter turn; this procedure must be continued for a total of 15 minutes. Be careful not to damage or lose the wire mesh screens during handling. Place screens on Kimwipes to dry.

Precoated Filters for Ozone Measurement

Precoated filters ordered from Ogawa and Co. arrive in glass vials labeled with the filter count and the date coating occurred. Typically, filters from a single order are prepared as one lot. They must only be stored in their original containers. Store the vials refrigerated at 5 °C. Glass vials must only be opened in the protective environment of the glovebox containing air purified of ozone. When a batch of filters is kept at room temperature for field use (see section "Study Design Considerations"), they should be stored in a cool, dark place.

For quality assurance, a set of blanks handled in the glovebox should be analyzed prior to a study to ensure that glovebox protection is adequate. If not, further measures should be taken, such as running the glovebox under positive pressure with air filtered through GI charcoal.

To minimize the risk of temperature swings or possible mishandling during shipment, unexposed filters are shipped overnight delivery. Protect filters from direct contact with water droplets; thus, ensure all sampler parts are completely dry before assembly, forceps are wiped dry after cleaning, etc.

As a coated filters age, some conversion of nitrite to nitrate occurs. To minimize this "background," filters must be used as soon after coating as possible. At present, shelf life of unrefrigerated filters is conservatively 4 weeks from the coating date to the analysis date (after exposure). If necessary, analysis 6 to 8 weeks after coating could safely be performed. Shelf life of refrigerated coated filters is currently being investigated. Until refrigeration shelf life is determined, successive shipments of precoated filters are necessary for long-term field studies .

Assembly of the Ogawa Passive Sampler

Glovebox preparation. Assembly of the badges must take place in the large chamber of the glovebox. Prepare the glovebox by placing a large Kimwipe over the filter paper floor of the glovebox. (The Kimwipe should be thrown away after assembly.) Inside the glovebox, have ready: Milli-Q water in a small washbottle, both types of forceps, razor blade, and supply of small Kimwipes. Assembly can be done with clean, dried hands, which must never touch the filters. Labgloves are unnecessary. Forceps used for handling the precoated filters must be wiped clean with a Kimwipe moistened with Milli-Q water. Keep the forceps on a small Kimwipe off to the side,

designated as a "clean" area.

Ogawa sampler parts. Outside of the glovebox, place an ID label on the back of each pin-clip for each sampler to be assembled. Inside the glovebox, arrange the following: beaker of clean screens, beaker of clean cylindrical bodies, beaker of clean diffusion endcaps, pin-clips, resealable bags, and vial of precoated filters.

Sampler Assembly. The following outlines the assembly steps for each sampler. Use the blunt forceps whenever possible to prevent filter damage. Note that two filters must be assembled into each sampler, one at either end of the sampler body.

1. Select a cylindrical sampler body. For ease of assembly, turn the body upright so that it sits on an open end on a clean surface. A small Kimwipe could be used for this surface. Alternatively, the body can be gripped between two fingers.

2. Using the forceps, place one of the stainless screens in the upright well. Be careful not to bend or damage the screen, and make sure that it sits flat on the Teflon spacer ring at the bottom of the well.

3. Open the vial containing the precoated filters. use forceps to gently grip one of the filters by its edge. Notice that the sides of the filter have different textures. One side is rough, the other side is woven and has a waffle-like appearance. Place the filter in the well, rough side up. Again, be careful not to damage the filter and watch that it sits flat against the stainless screen. If a filter is dropped, get another from the glass vial.

[Note: Keep the vial containing the precoated filters loosely covered with its cap during the assembly process. Immediately recap when done.]

4. Place a second stainless screen over the precoated filter, taking the same precautions as before.

5. Pick up a diffusion endcap by its edge. Avoid touching its flat sides. Secure an endcap into the well. If the endcap is slightly loose, the retaining ridge on the pin-clip should hold it in place.

6. Next, flip the body of the badge over and repeat directions 2 through 5 to insert a coated filter in the opposite well. When doing this, grip the sampler body between two fingers.

[Note: If assembling samplers individually, grip the sampler bodies with your fingers. If an "assembly line" approach is preferred for several samplers at once, lay clean small Kimwipes and place a row of sampler bodies upright on the Kimwipes.]

7. After assembling the body of the sampler, snap the body into a pin-clip holder and place the completed badge into a resealable bag. Expel the air from the bag and seal it.

8. When a group of samplers are assembled, bring amber storage bottles and caps into the glovebox. Place each bagged assembly into a bottle, cap it, and tape the cap on. Remove the amber bottles from the glovebox.

9. Place the matching ID label on the outside of the storage bottle. Use lab tape to secure the cap. The sampler is now ready for ozone monitoring.

3.2. Sampler Packaging, List of Items

The Ogawa samplers need to be shipped to the park locations just prior to their use for sampling. Shipping dates and label codes will be given in documents covering each study. Ship two extra "blanks" with each mailing to serve as spare samplers in case samplers are damaged during shipment or when being mounted in the rainshields on-site.

Materials needed for shipping:

shipping box, packing material ("worms" or bubble-pak), shipping labels
shipping document listing contents
sample log sheets, one per sample (see section 3.4)
return labels, shipping documents with billing to Contractor's account, (overnight shipment)

3.3. Labeling the Samplers

Prior to shipment each sampler will be labeled according to the scheme below. Labels should be attached to the Ogawa sample device not to the storage vial. In addition, the storage vials should be color code with tape for easy identification in the field according the chart below. The tape can be used to seal the lids to the plastic vials to prevent them from coming off during shipment.

Color coding for the vials:

Sampler for exposure	color determined by project
Blanks (not exposed)	black tape
Extra samplers	green tape

The samplers will be labeled according to the codes below:

Code:	week	site	number	type	
	# -	####	##	#	
	1,2	GSUP	1-5	A	
	etc.		etc.	A, B	Sample, duplicate
				Blk	Blank

3.4. Sample Report Forms (SAMPLE)

Park: GRSM ⇒ **Site:** GSUP ☐ GSLR ☐ GSCM ☐
SEKI ⇒ SEGG ☐ SELK ☐ (Check box for site)

SAMPLE ID: __ - _____ - . _____

1. **START DATE:** ___/___/___ (MMM DD YY) 2. **START TIME:** ___:___ (HH MM)

3. **END DATE:** ___/___/___ (MMM DD YY) 4. **END TIME:** ___:___ (HH MM)
(Note: Use 24-hour clock and local standard time)

5. SHIPPING CONTAINER CLOSED UPON ARRIVAL? YES NO (Circle one)
If NO then write "Sample Invalid" under item 8 below and on sample

6. ENVIRONMENTAL CONDITIONS: Answer "YES" or "NO" for each question. If a) or b) is "NO" or c), d), e) are "YES" then describe fully under item 7, Sampling Notes.

	Yes or No ?
a. Sampler/rain shield intact?	
b. Support tee in original position?	
c. Heavy rains w/strong winds during sampling period?	
d. Raining when sampler was changed?	
e. Sampler wet at any time?	

7. SAMPLING NOTES: _____

8. ADDITIONAL COMMENTS: _____

9. OPERATOR NAME: _____ 10. TODAY'S DATE: ___/___/ 93

LAB USE ONLY

DATES: SAMPLER OUT _____ SAMPLER IN _____

SAMPLER INTACT ? **Y N** CONTAINER INTACT? **Y N** SAMPLE SUSPECT? **Y N**

COMMENTS : _____

QA FLAG: _____ INITIALS: _____ QA CHECK: _____

1993 STUDY SITEFORM.DOC
FORM NO. NPS/AQD-PSS-2

3.5. Laboratory Record Keeping of Sample Handling

Records will be kept indicating when filters were received, when Ogawa samplers were loaded, the shipping and return dates of the samples, the extraction dates, and the IC analysis dates. These records will be included in the final data report.

4. Analysis Procedures

4.1. Unloading and Storage Procedures

from HSPH:

Part 2. Disassembly of the Ogawa Sampler After Exposure

Equipment

After sampling, the badges will be disassembled and filters removed in the laboratory glovebox. The following supplies in addition to those listed for sampler assembly, are needed for this process:

Extract vials (HDPE, 8 mL capacity, leakproof with screwcap, inert)

Beakers (1 each for used screens, used diffusion endcaps, used sampler bodies.

Safety razor blade

Petri dish

Glovebox preparation. Use the same preparation as for assembly. Clean forceps as previously described. Thoroughly clean the new razor blades with alcohol. (Use Milli-Q water and a Kimwipe thereafter.) Have ready in the glovebox: extract vials, extract vial screwcaps. Arrange the three beakers. Allow for a space in the rear of the glovebox where resealable bags and pinclips can be piled. Note that samplers must be disassembled one-by-one, and forceps must be wiped clean between samplers.

Extract Vial Preparation. Extract vials must be thoroughly rinsed at least three times with Milli-Q water. Shake excess water from the vials and screwcaps. Lay on Kimwipes to dry. Cover with a single layer Kimwipe to protect from dirt and dust while drying. When completely dry, screw the cap onto the vial to keep the interior clean.

Sampler Preparation. For a group of samplers which can be disassembled in the glovebox at one time (6 to 10 samplers), remove the bagged samplers from their amber storage bottles. Immediately place the bagged samplers in the glovebox.

Sampler Disassembly. The following outlines the disassembly steps for each sample. An "assembly line" process is discouraged, because sample IDs may be confused.

1. Take the sampler out of its resealable bag. Remove the sampler body from the pin-clip.

2. Select an extract vial. Remove the label from the pin-clip and affix it to the extract vial. Loosen the cap of the extract vial. Discard the bag and pin-clip to the rear of the glovebox.

3. Grip the sampler body with your fingers, orienting it upright. Avoid touching the flat surface of the diffusion endcaps. Remove the top endcap of the sampler body, handling it at its edge. Place in endcap beaker.

4. Tilt the body such that the top screen begins to fall at an angle; however, use the forceps flat against the well to prevent the screens and filter from falling out. (Sometimes light tapping with the forceps against the well is necessary to dislodge the screens and filter.)

5. Grab the edge of the top screen and remove it. Again, tilt the sampler body until the filter leans out of the opening. Gently, remove the filter using the forceps. (If possible, it can be easier to remove the filter from between the screens if the three disks fall away from each other.) If necessary, the clean razor blade can be used to separate the filter from the screen.

If the filter accidentally falls to the flooring, note on logsheet. (The filter must still be analyzed.) To prevent contaminating a dropped filter, make efforts to keep the surface clean directly below the held sampler body.

6. Place the filter into the extract vial. If the filter does not insert easily, then the filter may be folded by using second pair of clean tweezers. Replace the cap loosely on the vial.

7. Flip the sampler body over and repeat steps 3 through 6 to remove the second filter. Be sure to place the second filter in the same extract vial as the first filter.

8 Repeat the process for each sampling badge. Be sure to wipe the forceps clean after handling each sampler.

[Note- To prevent against dropped filters when first learning to disassemble the Ogawa sampler, disassemble the sampler above a clean petri dish. With the forceps, gently allow the filter and screens to fall onto the petri dish. Do this for both sides of the sampler, and place the filters into the extract vial. Place the used screens in the appropriate beaker. The petri dish must be wiped clean with a dry Kimwipe between samplers.]

9. Store the extract vials of dry filter pairs from each sampler at 5°C in the dark until analysis.

4.2. Analysis Procedures

from HSPH:

Part 3. Ion Chromatographic Analysis of the Passive Ozone Samples

Equipment

To prepare the filters for analysis by ion chromatography using a Dionex 2000i or equivalent, the following equipment and supplies are needed.

Automatic pipet (5 mL)

Glovebox (with $NaNO_2$-coated filter paper flooring), OR

Positive pressure hood, supply air filtered through GI charcoal

IC vials (0.5 mL for Dionex autosampler)

Caps for IC vials

Syringes, 3 mL disposable

Syringe filters

Ultrasonic bath (sonicator) with support rack for extract vials

Filter Preparation

IC vial preparation. Vials must be thoroughly washed with Milli-Q water, completely dried in room air while covered with Kimwipes, and stored in clean covered containers. (Vial caps used by HSPH require no further cleaning.)

Filter extraction. The following steps outline the extraction process. Since exposed filters are more stable when stored dry in the extract vials, extract only the number of samples that can be analyzed at one time

1. Introduce 5 mL of Milli-Q water into each extract vial using a calibrated automatic pipet. This procedure must be done in the glovebox or positive-pressure hood.

2. Just prior to analysis, each of the samples in the extract vials must be sonicated in an ultrasonic water bath.

    a. Check that the filters in each extract vial are completely immersed in the aqueous solution. If not, then use a clean, stainless steel spatula or forceps to depress the filters into the aqueous solution. Be sure to wipe the forceps clean between samples.

    b. Place the extract vials on a rack in the ultrasonic bath.

    c. Sonicate the extract vials for 5 minutes, rotate the rack 90 degrees clockwise; repeat the rotation twice for a total sonication time of 15 minutes.

3. Use a new, clean 3 mL disposable syringe to remove a portion of a sample from the extract vial.

4. Attach a new, clean syringe filter unit onto the syringe.

5. Transfer the sample into an ion chromatography vial (IC vial).

6. Repeat steps 3 through 5, for each extract vial sample. Remember to use new, clean syringes and filter units for each sample extract.

7. The samples are now ready for nitrate analysis by ion chromatography.

[Note; For every 7th (or lOth) sample, prepare two IC vials with the same syringe and syringe filter, for replicate analysis.

Ion Chromatography Analysis

The following outlines the operating specifications for Ozone filter IC analysis at HSPH. The

specifications are listed here for informative purposes only, and are not meant as absolute guidelines for ozone filter IC analysis performed by laboratories other than HSPH.

Instrument: Dionex Series 2000i or DX-300 Conductivity Detector:

Anion eluant flow - 1.7 mL/minute
Nitrogen: NF grade @ 100 psi
Eluant pressure - 5 psi
Regenerant pressure - lO psi
Detector range - 10 uS
Conductivity baseline - 14.0 to 16.0 (14.7 - 15.3) uS

Columns: Separator Column #AS4A (Cat # 37041)
Guard Column #AG4A (Cat # 37042)
Anion MicroMembrane Suppressor Model #AMMS-l

Eluant/Regenerant:

Until February l992/ HSPH used this anion eluant:

For 10 L total:

50 mL 0.36M Na_2CO_3
50 mL 0.34M $NaHCO_3$
9900 ml Milli-Q water

(1.8 mM Na_2CO_3, 1. 7 mM $NaHCO_3$]

At the suggestion of Dionex, HSPH began using a dilute anion eluant to further separate the nitrate peak from the much larger nitrite peak. The preferred dilute anion eluant is now:

For 10 L total:

20 ml 0.36M Na_2CO_3
20 ml 0.34M $NaHCO_3$
9960 ml Milli-Q water

[1.08 mM Na_2CO_3, 1.02 mM $NaHCO_3$]

Eluant stock solutions:

Conc. Anion Eluant: 0.34 M $NaHCO_3$
(28.6 $\pm$ o.1 g $NaHCO_3$ in 1 L Milli-Q water)

Conc. Anion Eluant: 0.36 M Na_2CO_3
(38.16 g Na_2CO_3 in 1 L Milli-Q water)

Regenerant: 11.1 mL of conc. H_2SO_4 (36 N), total to 10 L

w/Milli-Q water (to give 0.040 N H_2SO_4)

Standards. Nitrite, nitrate, and sulfate ion are detected by the ion chromatography configuration outlined above. In filter analysis, nitrite is an especially large peak since it is the basis of the coating solution. It is necessary to distinguish between the nitrite and nitrate peak, particularly when blanks are analyzed which have low nitrate levels. Since the analysis of exposed filters display these three peaks, the anion working standards contain all three ions. ("Standard #" refers to an in-house laboratory numbering system. The solution concentration, ppm, is mg/L.)

Standard #	ppm Sulfate	ppm Nitrate	ppm Nitrite
4	10	8.0	8.0
5	4	3.2	3.2
6	2	1.6	1.6
7	0.8	0.64	0.64
8	0.4	0.32	0.32

Additional documentation

Other protocol documents written and used by Exposure Assessment and Engineering with respect to IC analysis are listed below. They are available on request to complement this protocol.

"Operation Procedures for the Dionex 4000i Ion Chromatograph," Appendix A11.8.4, Revision 6-19-89

"Calibration Procedure for Automatic/Dispensing Pipets," August 29, l989 version.

4.3. Quality Assurance/Quality Control

All sampling and laboratory analysis will be conducted in adherence to standard protocols for the operation of ion chromatographs. Site operators will adhere to field operating procedure and instructions developed specifically for this study.

Laboratory quality control procedures used for the analysis of the NPS SO2 filter pack samples will be followed. These procedures include the comparison of the regression parameters for the IC calibration curve performed prior to each run with those obtained in the past; analysis of a quality control sample at the beginning of every analytical run; analysis of a duplicate sample, spiked filter extract, and a calibration check standard every 20 samples or daily; inclusion of an EPA QA sample with each run. Additionally, five percent of the samples will be run in duplicate for the determination of analytical precision. All standards will be prepared using AC reagent grade or better chemicals. All results from the quality control checks, calibrations, and precision checks will be reported in writing with the final report.

5. Analysis Reporting Requirements

5.1. Records and Forms

Records will be kept indicating when filters were received, when Ogawa samplers were loaded, the shipping and return dates of the samples, the extraction dates, and the IC analysis dates. These records will be included in the final data report.

All results from the quality control checks, calibrations, and precision checks will be reported in writing with the final report.

All sample log sheets will be forwarded to the Air Resources Division with the final data and report. Electronic transfers of data by email or FTP are encouraged.

5.2. Reporting Sample Analysis Data

Within 15 days from the date of analysis, results of the analysis will be made available for each batch of passive samplers analyzed. A monthly final report summarizing all batch analyses is due by the 7th day of the next month; the Contractor will provide the forms and records above plus the analysis data for the samples in written form. In addition, results from the analysis will be reported in an ASCII format readable by a PC computer running MS Windows and, if possible, in a Excel spreadsheet format.

Correct format for submittal of data as an MS Excel worksheet is available as the attachment file "passive O3 report sample.xls".

6. Contacts

Ogawa & Co, USA, Inc. 1230 S. E. 7th Ave. Pompano Beach, FL 33060 (305) 781-6223 Don Schaeffer http://ogawausa.com/passive.html	supplier of sample devices & filters
Dr. John D. Ray, Atmospheric Chemist Air Resources Division - AIR National Park Service P.O. Box 25287 Denver, CO 80225-0287 (303) 969-2820 Fax (303) 969-2822	Principle Investigator/Project manager
http://www2.nature.nps.gov/ard/gas/passives.htm	NPS information site on passive ozone program

7. List of Materials and Equipment

I. Materials provided by NPS:

Ogawa samplers, badge holders, shipping/storage vials, rainshields

Standard Operating Procedures

Project plans and schedules for each project

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II. Materials and Equipment NOT provided by NPS:

Glove box (ozone-free atmosphere container), ozone traps & air delivery system

Ogawa coated-filters

Shipping materials

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